



Theoretical elucidation of acetylation of glycerol with acetic acid and acetic anhydride

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ABSTRACT

Density functional theory calculations on level of B3LYP functional and 6-31G** basis set are carried out on glycerol esterification reactions. The most stable structures of the reactants, intermediates and products are located by considering a large amount of conformers. The thermodynamics is discussed in terms of the calculated reaction Gibbs free energy. The glycerol esterification with acetic acid is found to be thermodynamically resisted, while its esterification with acetic anhydride is preferable with significantly exothermal property. This agrees well with experiments. The proposed process art has been experimentally and theoretically proved to be with low production costs and high head product selectivity.

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1. Introduction

Glycerol is the main byproduct of the biodiesel production by transesterification of oil with methanol. The world production of glycerol has been rising significantly leading to lower market prices, which makes glycerol a particularly attractive molecule for the synthesis of other value chemical products [1]. Glycerol molecule is symmetrical and has many rotamers with intramolecular hydrogen bonding, but the OH groups can be esterified into other derivatives [2]. For example, the glycerol is esterified by acetic acid and these esterification products can be a good alternative for the glycerol produced by biodiesel.

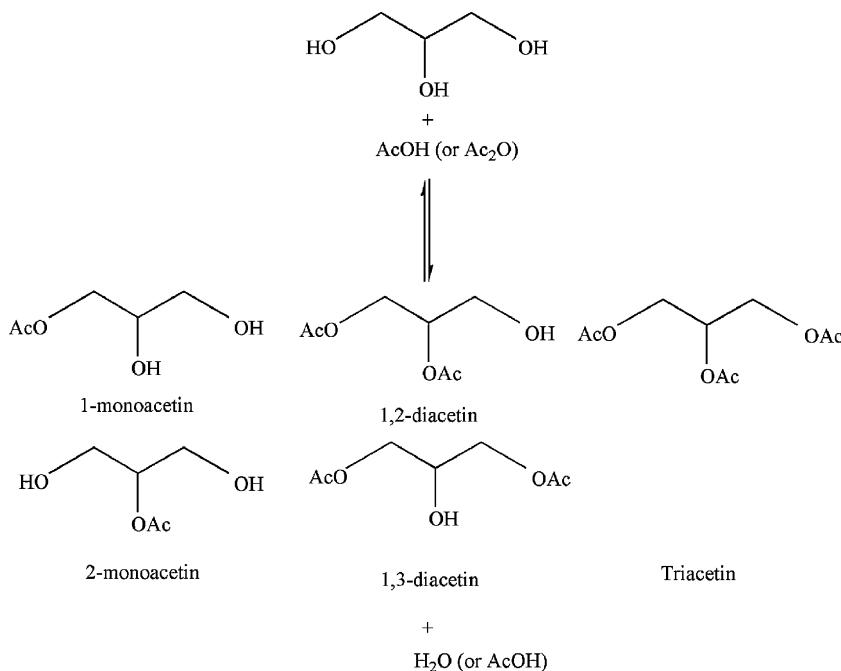
The products of glycerol esterification with acetic acid are monoacetyl (1-monoacetyl; 2-monoacetyl), diacetin (1,3-diacetin, 1,2-diacetin) and triacetin (Fig. 1), which have great industrial applications. The monoacetyl are used as a food additive and in manufacturing explosives and smokeless powder [3], also are valuable in pharmacochemistry and preparation of a specific antidote [4]. The diacetin has been utilized as a cocoa butter blooming agent or as an intermediate in the synthesis of structural

lipids [5], also is used for plasticizercoating and foodstuffs [6,7]. The mixture of monoacetyl and diacetin, have applications in cryogenics and biodegradable polyesters [8], chemical products in the food [9] and cosmetic industries [10]. In terms of triacetin, apart from its use as fuel additives for increasing the octane number in gasoline [11], it also has applications in cigarette filters and gelatinizing agent [3]. Mixtures of the substituted derivatives (mono-, di-, and triacetins) have many other applications: as solvents for printing ink and dyestuffs, as plasticizers, and as softening agents [3].

Although there are so many applications for acetylated glycerol derivatives, only a few reports have been found dealing with esterification of glycerol with acetic acid [12–14]. These works mainly focused on maximizing the di- and triacetin [12] or product distribution over solid catalyst [13–15]. Goncalves et al. suggested that the yield of di- and triacetylated glycerol increased with increasing conversion of glycerol and reaction time [13]. Research by microwave method showed that the Starbon acid had unprecedented high selectivity of mono- and diacetin [14]. Latterly, Ferreira et al. found good selectivity of diacetin could also be achieved over zeolite supported dodecamolybdophosphoric [15,16]. Above studies always obtained the mixtures of mono-, di- and triacetin. In fact, the substituted derivatives (mono-, di-, and triacetins) have close boiling points, which makes the separation process is very difficult and costly. In the most recent, 100% selectivity of triacetin was achieved in high molar ratio (acetic acid/glycerol 24:1) and high pressure (200 bar) with

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**Fig. 1.** Products of glycerol esterification or acetylation.

Amberlyst-15 catalyst. Interestingly, 100% monoacetin was obtained if no catalyst was used at same condition [17].

Our recent experimental work has shown an idea of producing triacetin as additives of biodiesel from glycerol which is mentioned above a byproduct of biodiesel. Using Amberlyst-35 as catalyst, at ambient pressure with molar ratio of acetic acid/glycerol 3:1, nearly 100% selectivity of triacetin was obtained with 100% glycerol conversion by two steps: esterification and acetylation [18]. Conventionally, the esterification reaction is equilibrium-limited [19], so selectivity of triacetin has been poorly described in literature using heterogeneous catalysts (e.g., less than 8% in Ref. [16]). However, the selectivity of triacetin abruptly reaches 100% when the acetylated reagent (acetic anhydride) is added and the detail reason is unclear. We have tried to explain the phenomenon by thermodynamics, but the thermodynamics date of some substituted derivates (e.g., 1,3-monoacetin, triacetin) are unavailable in handbooks or databases directly or indirectly. Fortunately, an alternative method, i.e., the density functional theory (DFT) calculations could be used to obtain these data.

Indeed, the theoretical study of glycerol structures and interaction with organic in the gas-phase constitutes a very active domain of research. These researches have devoted to the configurations of glycerol [20], and its interaction with metals, as well as its hydrogenolysis over acid catalysts [21,22]. Recently, increasing attention has been paid to studies reaction of glycerol (or its derivatives). By DFT method, Asakuma et al. researched on transesterification of triglycerides and found that the ester bond at the center of the triglyceride is transesterified before peripheral ester bonds [23]. On the contrary, Jamroz et al. had done simulation work of etherification of glycerol and extrapolated that the substitution of glycerol are preferred at the terminal positions rather than at the central C–O group [24].

To our knowledge, there were no reports on the esterification of glycerol with acetic acid/acetic anhydride by theoretical calculation. Besides, many experiments didn't distinguish two kinds of monoacetins (1-monoacetin; 2-monoacetin) and diacetins (1,3-diacetin; 1,2-diacetin) [12–14]. In this paper, we locate the most stable structures of all acetylated glycerol derivates and mainly elucidate high selectivity of triacetin of our two-step art by theoretical calculations.

2. Calculation methods

Because a low temperature is used for the reaction, the reactants and products are all in liquid phase. There are also catalysts used. Therefore, this is a complex reaction for theoretical simulation. Generally, to elucidate the reaction process, a model needs to be prepared to describe the solid–liquid interface. This needs much information on the structures of the catalysts and a large amount of computer power. During our experimental tests, a very reactive Amberlyst-35 catalyst has been used, and the reaction reaches equilibrium within 30 min. Therefore the selectivity of monoacetin, diacetin and triacetin are determined by thermodynamics of the reaction after 4 h. This means the reaction mechanism at the catalyst surface is not interested in our calculation. The free molecules of the reactants and products were calculated to elucidate the problem.

All calculations were done with the Gaussian 03 program. All the discussions were at the level of B3LYP/6-31G** [25]. The B3LYP functional has been proven to predict with great accuracy the relative energies and structure for the most significant conformers of gas phase glycerol molecules [20,26,27]. The combination of the B3LYP functional with the 6-31G basis set had also been successfully applied recently to the study of five erythritol, threitol [28] and monosaccharides [29]. The frequency analysis at the same level determines the nature of stationary points, e.g., minimum structures without imaginary frequencies. This method was successfully used in previous works of our group [30].

3. Results and discussion

3.1. Searching the most stable configurations

This subsection will simply introduce the calculation of the structures and energies of the reactants, products and intermediates.

There are 126 possible conformers of glycerol [27]. Hadad et al. found that in the lowest energy conformer, the hydroxyl groups form a cyclic structure with three internal hydrogen bonds [22,27]. In our calculation, 126 possible conformers were calculated with AM1 method. The most stable structure determined from above

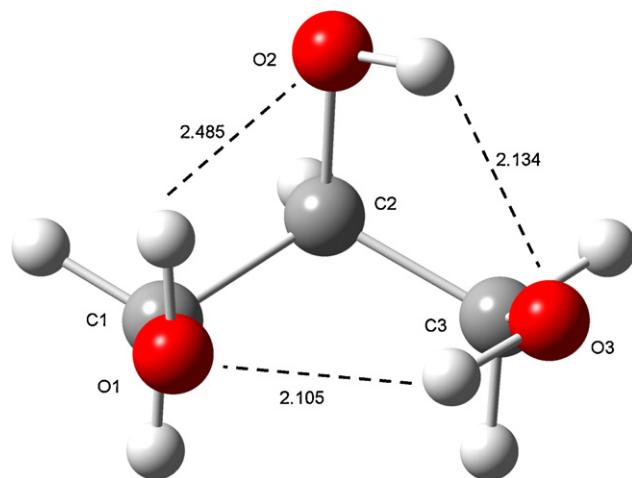


Fig. 2. The structure of glycerol (the red means oxygen atoms, the gray means carbon atoms and the white means hydrogen atoms).

calculations was further optimized at the level of B3LYP/6-31G**. The calculated structure is shown in Fig. 2. The three oxygen atoms of this isomer are in position, where favors the formation of three hydrogen bonds (2.105, 2.484 and 2.134 Å respectively) with neighboring oxygen atoms. The calculated length of hydrogen bonds agrees well with the results of Ref. [21] (2.103, 2.478 and 2.136 Å respectively).

The second step is to calculate the structures and energies of products (monoaceticin, diacetin and triacetin). In order to simplify the calculation, the optimized glycerol structure (see Fig. 2) was used as start structure. The 1-monoaceticin and 2-monoaceticin structures were built by substituting the one H of -OH of glycerol with one acetyl group (i.e., $-(\text{C}=\text{O})-\text{CH}_3$). Then all the possible structures (with rotating CH_3 group) were calculated at level of AM1 to locate the most stable structure. Then the most stable structures of 1-monoaceticin and 2-monoaceticin were refined at the level of B3LYP/6-31G**. The most stable structures of monoaceticin are shown in Fig. 3.

For diacetin, we used similar search scheme with monoaceticin. The structures in Fig. 3 were used as start structures, then one H of

$-\text{OH}$ was substituted with an acetyl group (i.e., $-(\text{C}=\text{O})-\text{CH}_3$). After calculating with AM1 method and refining with B3LYP/6-31G** method, the most stable structures of 1,2-diacetin and 1,3-diacetin were located and shown in Fig. 4. With similar scheme with monoaceticin and diacetin, the most stable structure of triacetin was located and shown in Fig. 5.

3.2. Product distribution

Table 1 shows the product distribution of glycerol esterification with acetic acid experimentally measured in this study. The reaction is performed in round-bottomed flask, and reaction condition is given as follow: $T = 105^\circ\text{C}$, $t = 5\text{ h}$, acetic acid/glycerol = 0.6 mol:0.1 mol, without catalyst. We can find that the amount of 1-monoaceticin is 9.5 times to 2-monoaceticin. Similarly, from Table 1 we can see the difference of distribution between 1,3-diacetin and 1,2-diacetin is relatively small (5.5 times).

Mulliken population analysis has become the most familiar method to count electrons associated with an atom. It provides a means of estimating partial atomic charges from calculations based on the linear combination of atomic orbital molecular orbital method [31,32]. Esterification reaction is initiated by the transfer of a proton from the catalyst to the carboxylic acid [33]. It should be noted that the acetic acid has self-catalyzed ability for it can provide the proton if there are no other catalysts in this reaction. The proton attaches on the lone pair of the oxygen which is double-bonded to the carbon, and this causes the carbon obtain a fair amount positive charge. Then it is attacked by the negative charged hydroxyl group of the alcohol molecule [34]. As shown in Table 2, we can see that the O1 of peripheral $-\text{OH}$ have biggest Mulliken atomic charges (-0.4206 e), thus it has large nucleophilic affinity, so it is easier to attack the protonated carboxylic acid. Therefore the formation of 1-monoaceticin is competitive from the aspect of electronic structures. Another important competitive step happened between the two $-\text{OH}$ of 1-monoaceticin. As shown in Table 2, the atomic charge of O3 of $-\text{OH}$ is -0.1689 e , bigger than that of O2 (-0.1623 e). It means O3 is more apt to reaction with positive charge acid group. Therefore, formation of 1,3-diacetin is competitive than 1,2-diacetin.

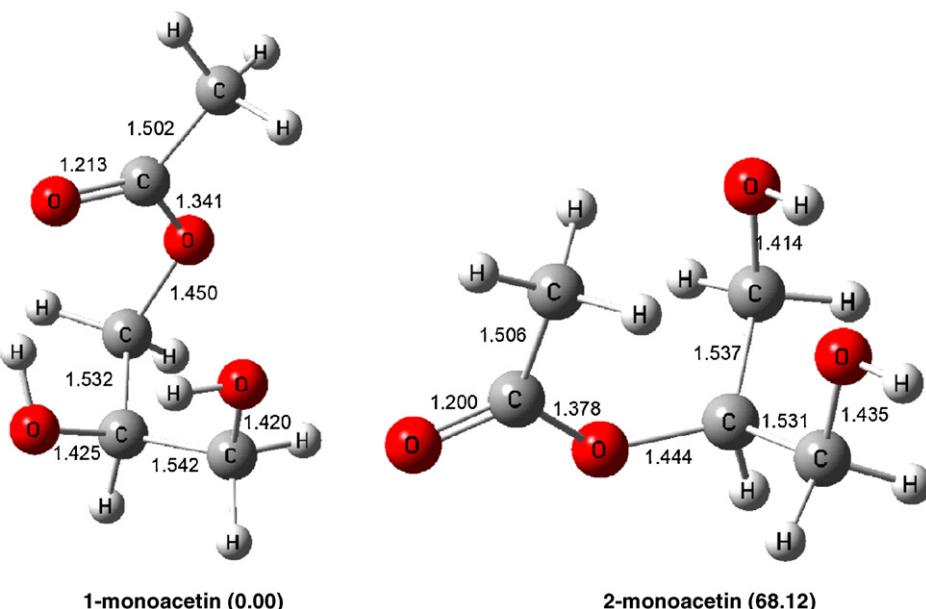


Fig. 3. The structures and relative energies (kJ/mol) of monoaceticin. The energies in the brackets are the electron energies corrected with zero point vibration energies relative to the most stable conformer (1-monoaceticin).

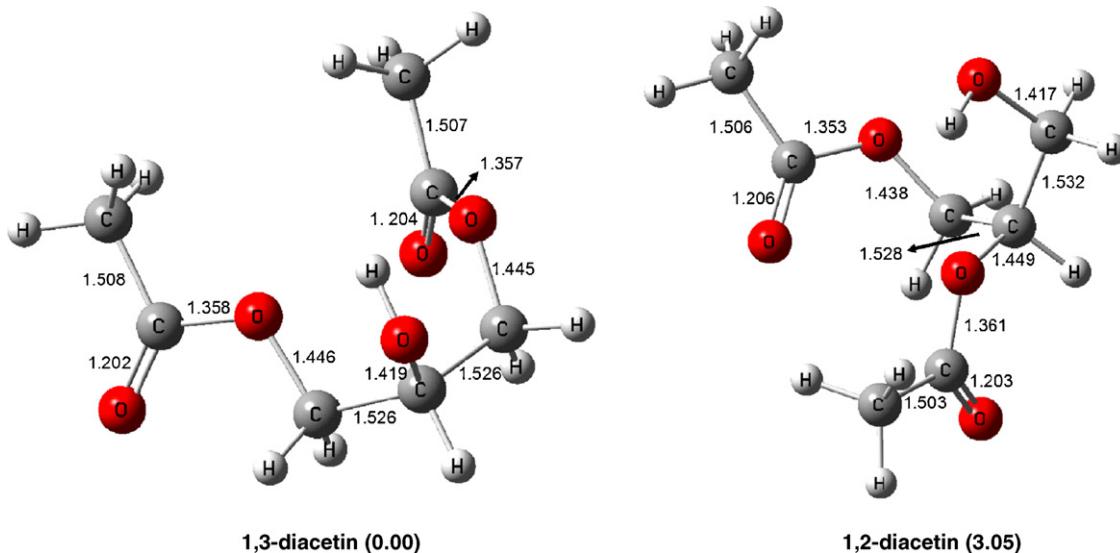


Fig. 4. The structures and relative energies (kJ/mol) of diacetin. The energies in the brackets are the electron energies corrected with zero point vibration energies relative to the most stable conformer (1,3-diacetin).

3.3. Thermodynamics of glycerol esterification with acetic acid

As mentioned above, our purpose is to optimize the selectivity of triacetin produced from glycerol. In this subsection, we will find out the reason for low selectivity of triacetin.

The thermodynamic scheme at 105 °C is shown in Fig. 6. The standard Gibbs free energies relative to the reactants (glycerol + 3AcOH) labeled in brackets. The energies of the most stable structures of each species are used when drawing Fig. 6. The standard reaction Gibbs free energies of the three steps of esterification reaction are all positive, this indicates that the reactions are thermodynamically resisted. The reaction Gibbs free energies of the first and second steps are relatively small (19.15 and 17.80 kJ/mol), while that of the third step is large to 55.58 kJ/mol. This quantitatively shows the reason for low selectivity of triacetin. It should be noted that the values of Gibbs free energies in this paper is standard values calculated under 1 bar pressure in gas phase. People could increase the conversion of glycerol and selectivity of monoaceton, diacetin and triacetin by using relatively large amount of the co-reactant acetic acid (acetic acid/glycerol ratio). However, it is not acceptable if the acetic acid/glycerol ratio

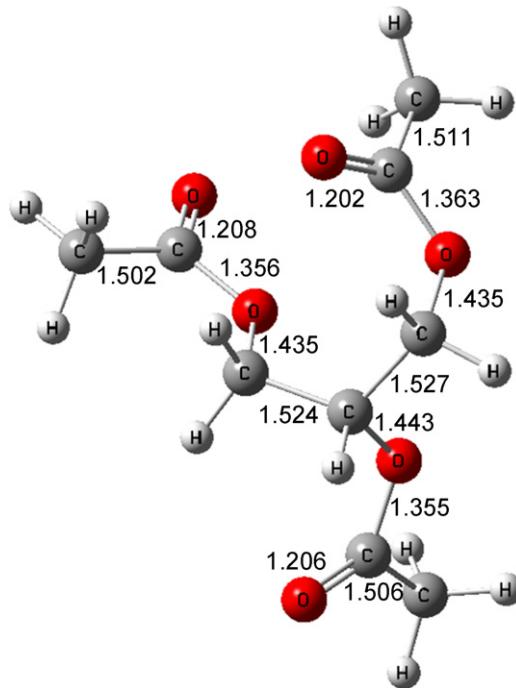


Fig. 5. The optimized structure of triacetin.

Table 1

Product distribution (%) ($T=105^{\circ}\text{C}$, $t=5\text{ h}$, acetic acid/glycerol = 0.6 mol:0.1 mol, without catalyst).

Product	Distribution
1-Monoaceton	65.7
2-Monoaceton	6.9
1,3-Diacetin	20.3
1,2-Diacetin	3.7

ol + 3AcOH) labeled in brackets. The energies of the most stable structures of each species are used when drawing Fig. 6. The standard reaction Gibbs free energies of the three steps of esterification reaction are all positive, this indicates that the reactions are thermodynamically resisted. The reaction Gibbs free energies of the first and second steps are relatively small (19.15 and 17.80 kJ/mol), while that of the third step is large to 55.58 kJ/mol. This quantitatively shows the reason for low selectivity of triacetin. It should be noted that the values of Gibbs free energies in this paper is standard values calculated under 1 bar pressure in gas phase. People could increase the conversion of glycerol and selectivity of monoaceton, diacetin and triacetin by using relatively large amount of the co-reactant acetic acid (acetic acid/glycerol ratio). However, it is not acceptable if the acetic acid/glycerol ratio

Table 2

The Mulliken atomic charges of oxygen.

	Mulliken atomic charges (e)		
	O1	O2	O3
Glycerol	-0.4206	-0.4143	-0.4150
1-Monoaceton	-0.1623	-0.1689	

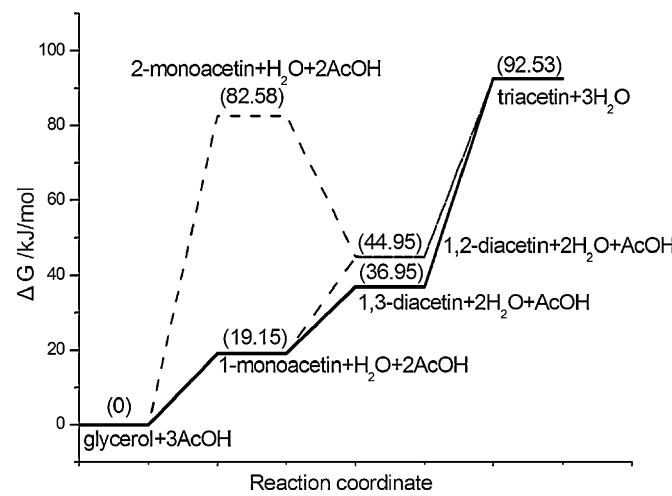


Fig. 6. Thermodynamic scheme (kJ/mol) of glycerol esterification with acetic acid at 105 °C.

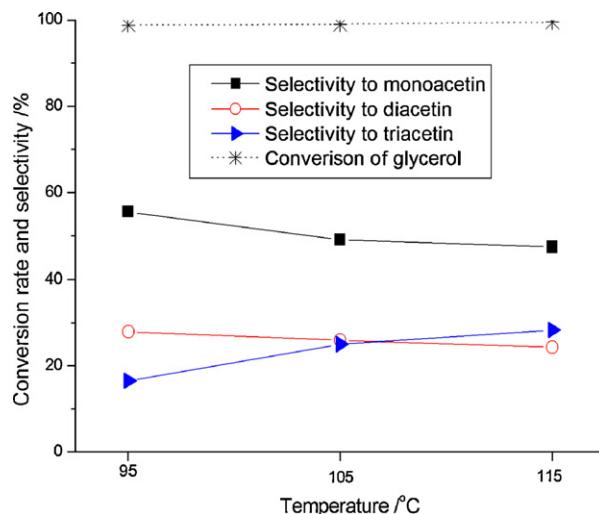


Fig. 7. Effect of temperature to the experimental selectivity and conversion rate. These data are allocated from Ref. [18] ($t = 4$ h, acetic acid/glycerol = 0.6 mol:0.1 mol, 0.5 g Amberlyst-35).

is too high on practical aspect. Also, it is quite difficult to reach satisfying triacetin selectivity (for the interested readers, please see ref [18]).

We then tried different reaction temperatures in order to change the equilibrium constant by shifting the reaction Gibbs free energies. Fig. 7 shows the results of the experimental test (from Ref. [18]). It was found that the selectivity did not change significantly. The theoretically calculated reaction Gibbs free energies at different temperatures are shown in Fig. 8. From the trend in both Figs. 7 and 8, we cannot see any hope for obtaining high selectivity of triacetin under mild temperature.

3.4. Thermodynamics of glycerol acetylation with acetic anhydride

There is another reaction which can transfer glycerol into triacetin, i.e., acetylation with acetic anhydride. We firstly built up a similar thermodynamic scheme in Fig. 9. It is seen that the reaction Gibbs free energies of all the three steps are negative, which means the reactions to produce triacetin via this pathway is preferable. However, the reaction is highly exothermal, and the calculated enthalpies of the three steps (ΔH , at 105 °C) are –58.17,

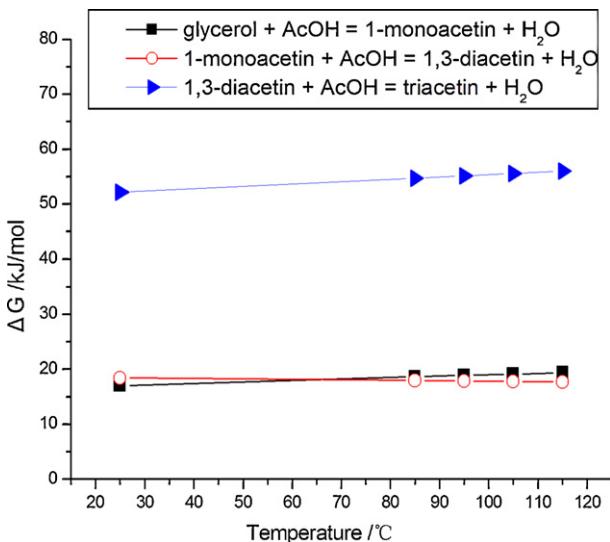


Fig. 8. Effect of temperature to the DFT-calculated reaction Gibbs free energies.

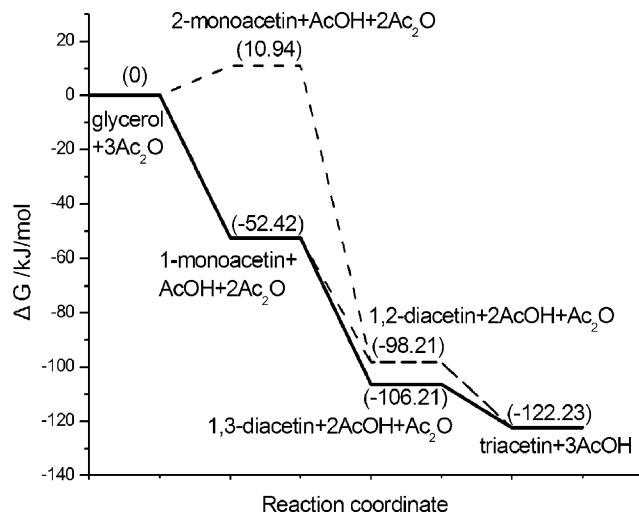


Fig. 9. Thermodynamic scheme (kJ/mol) of acetylating of glycerol with acetic anhydride at 105 °C.

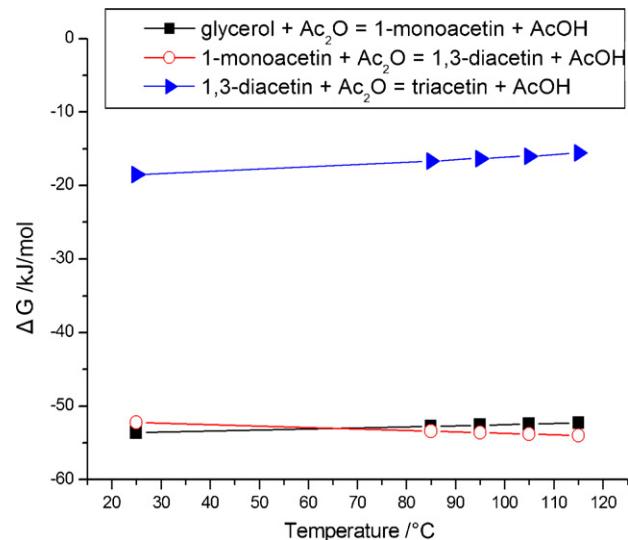


Fig. 10. Effect of temperature to the DFT-calculated reaction Gibbs free energies.

–46.28 and –28.03 kJ/mol, respectively. It indicates that the total reaction of producing triacetin by glycerol acetylation releases heats 132.48 kJ/mol. This is the reason for violence of the reaction. Fig. 10 shows that it is also impossible to significantly change the thermodynamic parameters by changing reaction temperatures. Even at ambient temperature, the reaction is also violent and impractical.

3.5. Combination of esterification and acetylation

Although the main results from the above investigation are negative, we have found some interesting information. The main product of glycerol esterification is monoacetin with relatively small amount of diacetin and triacetin [18], this is consistent with the calculated mild values of Gibbs free energies (19.15 and 17.80 kJ/mol) of the first and second steps. The glycerol acetylation can produce high selectivity of triacetin but produces too much heat. We noticed that the heat is mainly produced during the first step of acetylation reaction (–58.17 kJ/mol); the second step produces less (–46.28 kJ/mol), while the third step only produces a small amount of heat (–28.03 kJ/mol). An idea of combination of

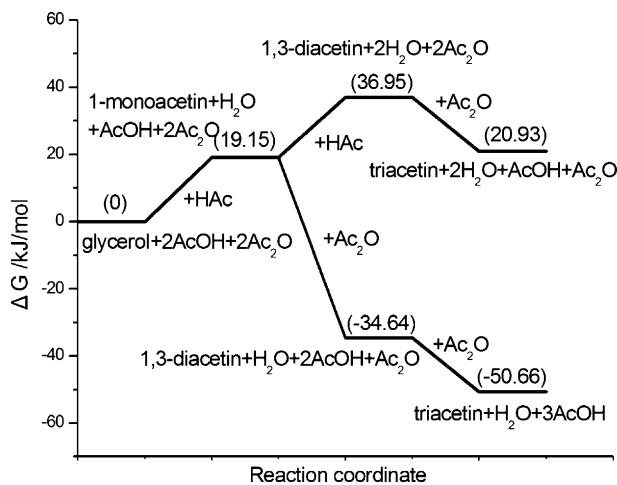


Fig. 11. Thermodynamic scheme (kJ/mol) of acetylating of glycerol with two-step art at 105 °C.

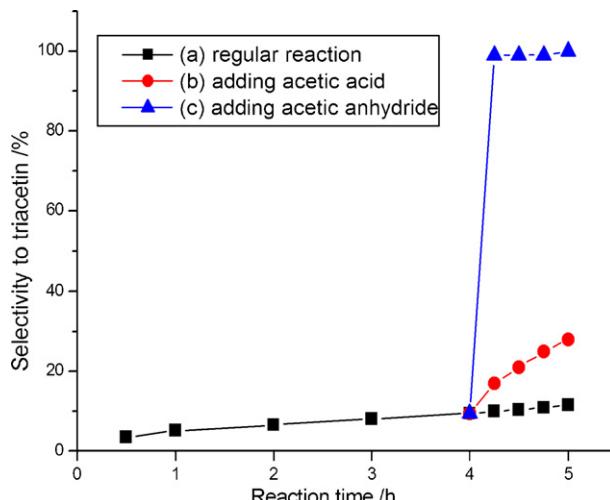


Fig. 12. Performance of two-step art. These data are allocated from Ref. [18].

the esterification and acetylation reactions is therefore theoretically tested.

Fig. 11 shows the thermodynamic scheme of the above-mentioned combination. The first pathway is glycerol esterification to produce monoaceton, and then monoaceton acetylation with acetic anhydride to produce triacetin. The reaction Gibbs free energy of the total reaction is -50.66 kJ/mol , which indicates that this reaction is preferable thermodynamically. The calculated reaction enthalpy is -64.69 kJ/mol , and this is a mild reaction. Another pathway is slightly uncompetitive, that is glycerol esterification into diacetin and then acetylation into triacetin. This pathway has reaction Gibbs energy of 20.93 kJ/mol . This pathway is slightly endothermic with reaction enthalpy of 3.09 kJ/mol . From the analysis, a perspective reaction has been designed.

In an attempt to maximize the triacetin, the two-step reaction has been tested experimentally, as shown in Fig. 12 (from Ref. [18]). It is found that the selectivity of triacetin obtains abruptly improvement if thereto acetic anhydride is added when the esterification reaction reaches its equilibrium. This indicates that the acetylating ability is considerably higher than that of the esterification. This is in line with thermodynamic scheme is given in Fig. 11. As mentioned above, the first step of acylation of glycerol gives a large amount heat. Avoiding much heat is given out at this step; the acetylation of glycerol has been instead with

esterification by acetic acid instead of acetic anhydride. Another consideration is the fact that a lowest cost of raw materials, for the price of acetic anhydride is higher (ca. four times) than that of acetic acid.

Based on the above reasons, the high selectivity of head product triacetin is facilely obtained at mild condition avoiding the high pressure (200 bar) and high molar ratio of acetic acid/glycerol (24:1) at supercritical CO₂ condition [17]. In sum, this two-step art makes whole process is proceed to high valuable additive triacetin with the lowest possible production costs, including the costs of raw materials and easy operation.

4. Conclusions

The thermodynamics parameters are calculated by Gaussian software to clarify behavior of esterification and acylation of glycerol. Firstly, formation of various esters by the addition of one or more ester groups was considered by semiempirical AM1 method. The relative energies and reaction Gibbs free energies are obtained by optimizing the chosen structures, and the analysis of Mulliken atomic charges shows the outside hydroxyl bonds in the glycerol are esterified before the center hydroxyl bond. The thermodynamics is discussed in terms of the calculated reaction Gibbs free energy. The glycerol esterification with acetic acid is found to be thermodynamically resisted, while its esterification with acetic anhydride is preferable with significantly exothermal property, this agrees with experiments. The proposed two-step art has also been experimentally and theoretically proved to be with low production costs and high head product selectivity.

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